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**Synthesis and Characterization of Site-Isolated Hexarhodium Clusters on Titanial Powder**

J. Goellner and B.C. Gates (U. California Davis)

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[Rh<sub>6</sub>(CO)<sub>16</sub>] was prepared on the surface of TiO<sub>2</sub> (calcined at 200 or 400 °C) by deposition from *n*-hexane solution and by a surface-mediated synthesis from TiO<sub>2</sub>-supported [Rh(CO)<sub>2</sub>(acac)] in the presence of CO at 1 atm and 100 °C. The cluster preparation and subsequent decarbonylation by treatment in He or H<sub>2</sub> were characterized by infrared and extended X-ray absorption fine structure (EXAFS) spectroscopies. Deposition from solution gave aggregated [Rh<sub>6</sub>(CO)<sub>16</sub>] on TiO<sub>2</sub>; removal of the carbonyl ligands led to destruction of the Rh<sub>6</sub> frame and sintering to give rhodium aggregates. In contrast, the reductive carbonylation of TiO<sub>2</sub>-supported [Rh(CO)<sub>2</sub>(acac)] gave site-isolated TiO<sub>2</sub>-supported [Rh<sub>6</sub>(CO)<sub>16</sub>] in high yield, paralleling the chemistry of rhodium carbonyls in neutral solutions and on neutral surfaces. Removal of the carbonyl ligands from the site-isolated clusters by treatment in H<sub>2</sub> at 300 °C led to rhodium aggregates, but decarbonylation in He at 300 °C gave site-isolated Rh<sub>6</sub> clusters on the TiO<sub>2</sub>. The first-shell Rh–Rh coordination number of these clusters was  $4.4 \pm 0.4$  with a bond distance of  $2.64 \pm 0.03$  Å. Thus, the clusters formed by decarbonylation of site-isolated TiO<sub>2</sub>-supported [Rh<sub>6</sub>(CO)<sub>16</sub>] are represented as octahedral Rh<sub>6</sub> (which has a Rh–Rh first-shell coordination number of 4). EXAFS spectroscopy indicates that the decarbonylated Rh<sub>6</sub> clusters on TiO<sub>2</sub> calcined at 200 °C have a small amount of carbon bonded to them, but no such ligands were indicated in the spectra of the Rh<sub>6</sub> clusters on TiO<sub>2</sub> calcined at 400 °C.